

A NEW RAPID VOLUMETRIC METHOD

FOR THE DETERMINATION OF

NIOBIUM

IN THE PRESENCE OF

TANTALUM

AND ITS APPLICATION TO

THE ANALYSIS OF NIOBIUM MINERALS

BY

CHARLES EDWARD TAYLOR, B. S., A. M.

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY IN THE FACULTY OF PURE SCIENCE
COLUMBIA UNIVERSITY

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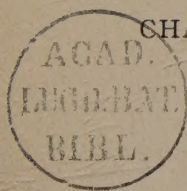
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ROBERTSON & WALLACE CO.
55 DEY ST., N. Y.

ACKNOWLEDGMENT.

This investigation was carried out under the direction and with the assistance of Dr. Floyd J. Metzger, for which I here wish to express my most sincere thanks and appreciation.

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March 1, 1909.

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INTRODUCTION.

The determination of niobium and tantalum, when existing together, has always been a stumbling block to the analytical chemist. The only method at present available is one based on the fractional crystallization of the double fluorides of these elements with potassium. The results by this method at best can be only approximate, as may be understood when the relative solubilities of these two double salts are considered. The solubility of the double potassium tantalum fluoride being given as one part of salt in 200 parts of water, whereas the corresponding niobium salt is soluble one part in 12.5 parts of water. Although with considerable experience and care duplicate analyses may be made by the crystallization method which show agreement, within about one per cent or even less, the values obtained do not represent the actual amounts of the elements present, as is reasonable to be supposed from the solubilities given above.

Osborne* describes a method for the determination of niobium and tantalum in the presence of titanium, which involves the reduction of the hydrochloric acid solution (containing a small amount of fluorides) of the combined elements, titration of the niobium and titanium, determination of the titanium colorimetrically, the tantalum being found by difference. But one determination is reported, which was made on a known mixture of oxides.

Warren* found the method of Osborne to be very inaccurate.

After a great deal of preliminary experimentation, it was found that, if succinic acid was added to a solution of niobium and tantalum in strong sulphuric acid, the solution could then be largely diluted, also heated, without precipitation of either the niobium or tantalum. This fact formed the basis of the work which follows.

* Am. Jour. Sci. (1885) **30**, 328.

* C. N. (1906) p. 298.

EXPERIMENTAL.

Use of Succinic Acid.

Inasmuch as succinic acid is not affected by potassium permanganate in acid solution, it was thought that the niobium might be reduced by zinc and acid and then titration made with potassium permanganate, and that the tantalum should remain unaffected by either operation.

Material.

The material used in this work was prepared from South Dakota Columbite, the niobium and tantalum freed from impurities by the usual method, then subjected to many recrystallizations, finally obtaining niobium and tantalum double fluorides of a high degree of purity.

Preliminary experiments showed that the niobium could readily be reduced when in sulphuric acid solution containing succinic acid, and could then be titrated by means of potassium permanganate solution, and that the presence of tantalum did not interfere.

Standardization of Solution.

The first experiments were made to determine the potassium permanganate standard in terms of Nb_2O_5 . The experiments were made as follows:

About 0.2 gram of Nb_2O_5 was fused with potassium bisulphate. The fusion treated with 40 c.c. of concentrated sulphuric acid by adding part of the acid to the crucible, heating to a clear solution, transferring the solution to a beaker and cleaning the crucible by washing with the remainder of the acid. Six grams

of succinic acid was then added to this concentrated sulphuric acid solution, which was then diluted somewhat with a saturated aqueous solution of succinic acid, and water added to a volume of 200 c.c., and while still quite warm (from dilution) passed through the reductor, followed by 200 c.c. of about 5% sulphuric acid, and titrated immediately with potassium permanganate solution.

Results are given in terms of Nb_2O_5 per c.c. of potassium permanganate solution used, and also, in the last column, the values converted to terms of exactly N/10 KMnO_4 .

No.	Nb_2O_5 Taken	Time minutes	KMnO_4 Required c. c.	Nb_2O_5 per c. c. of solution	Nb_2O_5 per c. c. N/10
(1)	.2224	7½	28.97	.007677	.00781
(2)	.2016	8½	26.20	.007702	.00783
(3)	.2338	7½	29.99	.007795	.00792
(4)	.2174	8½	27.21	.007699	.00782
(5)	.2174	10	28.22	.007704	.00783

The reductor used was 19 inches in length by ¾ inch in diameter, and was filled with amalgamated zinc.

A blank experiment containing sulphuric acid and succinic acid was made, and the deduction (0.1 c.c.) allowed.

These results, although not as uniform as might be desired, should not cause any serious error in the analysis of a mineral, and an attempt was made to determine the niobium in two samples of columbite, using the conditions given above for the reduction and titration.

The last two columns show the percentages of niobium and tantalum as found by the crystallization method.*

Mixtures of Niobium and Tantalum.

In view of the fact that the results for niobium were lower than those obtained by the crystallization method, it was thought that the presence of tantalum might have some influence on the reduction of the niobium. To test this assumption, known mixtures of pure Nb_2O_5 and Ta_2O_5 were tested with the following results:

No.	Ta_2O_5 Taken	Nb_2O_5 Taken	Time minutes	KMnO_4 c. c.	Nb_2O_5 Found
(9)	.2019	.1000	10	26.25	.2027
(10)	.1004	.1000	—	12.10	.0934
(11)	.1248	.2000	10	16.60	.1218
(12)	.0595	.2000	8	8.92	.0689

The results are irregular, (9) and (12) being high, and (10) and (11) low. It is evident, therefore, that the presence of tantalum does not interfere with the reduction of the niobium, for if it did the error would be uniformly in the same direction. A blank determination on the tantalum alone required only the 0.1 c.c. of KMnO_4 solution, which is the deduction for the zinc itself.

Atmosphere of Carbon Dioxide.

In view of these results, it was thought that possibly the reduced niobium might have become reoxidized by the air before

* For full description of this method see page 14.

titration. Hence the following determinations were made by adding solid sodium bicarbonate to the flask before reducing:

No.	Nb ₂ O ₅ Taken	Time minutes	KMnO ₄ c. c.	Nb ₂ O ₅ per c. c. of solution	Nb ₂ O ₅ per c. c. N/10
(13)	.2055	6½	27.1	.007583	.00770
(14)	.2059	—	27.5	.00748	.00780

These values are lower than those previously obtained (experiments (1)-(5), which means that the reduction was more complete. It was further observed in these two experiments that the solution in the case of (14) was considerably hotter than that of (13), and it was thought that the temperature should be maintained constant, which was done in the following experiments:

Temperature 75° C. 3 grams NaHCO₃ in flask.

No.	Nb ₂ O ₅ Taken	Time minutes	KMnO ₄ c. c.	Nb ₂ O ₅ per c. c. of solution	Nb ₂ O ₅ per c. c. N/10
(15)	.2426	8½	32.09	.007560	.007675
(16)	.2012	6	26.03	.007729	.00785
(17)	.2000	6	25.88	.007743	.00786
(18)	.2022	9½	26.60	.007601	.00772
(19)	.2071	6½	27.35	.007572	.007669
(20)	.1998	5	25.23	.007919	.00804

The results are still irregular.

At this point a different potassium permanganate solution was employed as well as a freshly amalgamated lot of zinc.

AMALGAMATION OF THE ZINC.

Considerably Amalgamated.

Temperature 75° C., 3 grams of sodium bicarbonate in the flask.

Titration were made as follows:

No.	Nb ₂ O ₅ Taken	Time minutes	KMnO ₄ c. c.	Nb ₂ O ₅ per c. c. of solution	Nb ₂ O ₅ per c. c. N/10
(21)	.2002	8	22.80	.008781	.008558
(22)	.2009	9	24.65	.008150	.007943
(23)	.2077	9	25.05	.008291	.008081
(24)	.2047	8	24.20	.008121	.007915
(25)	.2046	7	24.40	.008385	.008173
(26)	.2034	6	24.15	.008422	.008209
(27)	.2079	10½	24.10	.008626	.008408
(28)	.2115	8	24.15	.008758	.008536
(29)	.2086	9	23.75	.008792	.008569
(30)	.2054	9	23.10	.008688	.008469

In (25) to (27), inclusive, the solution was passed through the reductor at a boiling temperature instead of at 75° C.

These results, although very irregular, are considerably higher than have been obtained previously; that is, the reduction was less complete. It was further noticed that the reductor in the above experiments (21) to (30) was less active than in previous experiments, and it was assumed that the degree of amalgamation of the zinc might be of some significance.

Slightly Amalgamated Zinc.

Less mercury (the amount, however, not being weighed) was used in amalgamating the zinc employed in the following experiments:

No.	Nb ₂ O ₅ Taken	Time minutes	KMnO ₄ c. c.	Nb ₂ O ₅ per c. c. of solution	Nb ₂ O ₅ per c. c. N/10
(31)	.2051	13	28.10	.007300	.007114
(32)	.1988	14	27.30	.007281	.007096
(33)	.2046	15	28.55	.007166	.006984
(34)	.2074	16	28.45	.007290	.007105
(35)	.2129	16	29.30	.007266	.007082
(36)	.2018	16	27.25	.007405	.007218
(37)	.2121	17	28.90	.007337	.007152

These results show greater reduction of the niobium than any previously obtained, due, undoubtedly, to the fact that less mercury was used in the amalgamation of the zinc.

In experiments (34) and (35) an atmosphere of hydrogen was maintained throughout the reduction and titration. In experiments (35) to (37), as well as all experiments to follow, an atmosphere of carbon dioxide was maintained throughout the reduction and titration, employing a Kipp generator for carbon dioxide and a long-stemmed burette for the titrations.

Unamalgamated Zinc.

In view of the more complete reduction shown in the table above, where slightly amalgamated zinc was used, it was thought that perhaps there might be some advantage in the use of unamalgamated zinc in the reductor. Experiments were, therefore, made, filling the reductor with 20-30 mesh C.P. zinc, unamalgamated, but the action of dilute sulphuric acid was so very vigorous that the solution could not be drawn through the reductor sufficiently rapidly to prevent stoppage due to the matting together of the fine particles of zinc.

Conditions of Amalgamation.

It was now believed that, by adopting well defined conditions for the amalgamation of the zinc, uniformity of results might be obtained, and that these results would be more constant when the zinc is amalgamated only slightly.

The amalgamation of the zinc used in all experiments which follow was carried out in detail as described below.

Six hundred grams of 20-30 mesh C.P. zinc was amalgamated with a solution made by dissolving 0.5 gram of mercury in 25 c.c. of concentrated nitric acid and diluting to 250 c.c. with water. The zinc was shaken in this solution for several minutes, washed with water, then with dilute sulphuric acid, and kept under water until required for use in the reductor. The deduction for a blank on this zinc was 0.1 c.c. KMnO_4 solution.

Pure Oxides.

The supply of pure Nb_2O_5 having become exhausted, a new lot of material was prepared by taking two different samples of niobium salt and separating each of these into three fractions, which are designated in the table following as I_1 , I_2 , I_3 , and II_1 , II_2 , II_3 .

Procedure.

Inasmuch as every determination from this point was made in exactly the same manner, the exact details of the procedure are here given.

The oxide (or mixture of oxides) is fused with 5 grams of potassium bisulphate in a 30 or 40 gram platinum crucible. To the cooled mass 10 c.c. of concentrated sulphuric acid is added and heat carefully applied until a perfectly clear solution is obtained, which is allowed to cool, and the contents of the crucible transferred to a beaker, the crucible being rinsed with 30 c.c. of concentrated sulphuric acid. The solution should be perfectly clear at this point (any cloudiness shows incomplete fusion). Two grams of succinic acid is then added and the contents of the beaker stirred for a short time, about 20 c.c. of a saturated aqueous solution of succinic acid is then added in a fine stream from a wash bottle with constant agitation, then water is added to a volume of 200 c.c., and the solution heated to a temperature of 75° C. Meanwhile the reductor is prepared by passing through it 200 c.c. of 5% sulphuric acid heated to 75° C., rejecting this acid and filling again with 20% sulphuric acid heated to 75° C. The niobium solution is then passed through the reductor, followed by 50 c.c. of 20% sulphuric acid, and then by 200 c.c. of 5% sulphuric acid. The reduced solution, which is dark brown in color, is titrated with a standard potassium permanganate solution, the whole operation being carried out in an atmosphere of carbon dioxide. During the titration the solution first changes from brown to green, then through various shades of blue to colorless, the end-point being the characteristic color of the potassium permanganate. The end-point is very sharp. After each determination a few centimeters of the zinc is removed from the top of the reductor and replaced by fresh material, this being necessary, as otherwise a layer of finely divided zinc accumulates which would ultimately clog the reductor.

Different Samples of Oxide.

No.	Sample	Nb ₂ O ₅ Taken	Time minutes	KMnO ₄ c. c.	Nb ₂ O ₅ per c. c. of sol.	Nb ₂ O ₅ per c. c. N/10
(38)	I ₁ .	.2148	10	28.00	.007671	.007477
(39)	I ₁ .	.2051	16	26.60	.007711	.007515
(40)	I ₂ .	.2017	27	26.80	.007526	.007335
(41)	I ₂ .	.2012	31	27.50	.007316	.007131
(42)	I ₂ .	.2010	24	26.70	.007528	.007337
(43)	I ₂ .	.2033	37	26.90	.007557	.007366
(44)	I ₃ .	.2079	23	27.60	.007532	.007341
(45)	I ₃ .	.2031	35	27.05	.007508	.007318
(46)	II ₁ .	.2011	20	27.85	.007221	.007038
(47)	II ₁ .	.2012	28	27.95	.007199	.007016
(48)	II ₂ .	.1997	16	27.80	.007183	.007002
(49)	II ₂ .	.2048	16	28.00	.007314	.007129
(50)	II ₂ .	.2035	16	27.75	.007333	.007148
(51)	II ₃ .	.2012	16	27.50	.007316	.007131
(52)	II ₃ .	.2031	18	27.80	.007306	.007121
(53)	II ₃ .	.2077	12	28.45	.007301	.007116
(54)	II ₃ .	.2033	15	27.85	.007300	.007115

These results indicate highest purity for samples II₁ and II₂, while II₃ seems to show the presence of a slight amount of tantalum. All of samples "I" show the presence of a small amount of tantalum.

Purification of Oxides.

The above samples which indicate the presence of impurity were again purified as follows: All of samples "I" were combined, fused with potassium bisulphate, &c., as usual in the fractional crystallization of the double potassium fluorides. The solution of the double potassium fluorides was evaporated nearly to dryness, dissolved in the least amount of boiling water, and allowed to crystallize, yielding a crop of crystals which, upon careful examination, showed the presence of some needles of K₂TaF₇. The mother-liquor from these crystals was decanted through a filter and the crystals rejected. This mother-liquor was

evaporated to fumes with sulphuric acid, boiled with water, &c., as usual, obtaining finally the oxide, designated I_A .

Sample II_3 was purified in exactly the same manner as the combined samples "I" above, converting, however, both crystals and mother-liquor into oxide. That from the crystals being designated II_{3a} , and that from the mother-liquor II_{3b} .

Determinations were made on these samples with the following results:

No.	Samples	Nb_2O_5 Taken	Time minutes	$KMnO_4$ c. c.	Nb_2O_5 per c. c. of sol.	Nb_2O_5 per c. c. N/10
(55)	I_A .	.2015	6	27.90	.007221	.007038
(56)	I_A .	.2017	7	27.85	.007242	.007059
(57)	II_{3a} .	.2055	13	27.70	.007419	.007231
(58)	II_{3a} .	.2090	15	27.80	.007518	.007327
(59)	II_{3b} .	.2223	16	30.55	.007277	.007092
(60)	II_{3b} .	.2431	17	33.60	.007235	.007052

As was expected, sample I_A showed the effect of purification, giving results which agree, within the experimental error, with those of samples II_1 and II_2 . Similarly, sample II_{3a} indicates the presence of tantalum in the product, whereas sample II_{3b} showed the same degree of purity as samples II_1 , II_2 , and I_A .

Degree of Reduction of the Niobium.

The N/10 factor of the potassium permanganate solution was 1.0260.

$$1 \text{ c.c. of this solution} = .007232 \text{ } Nb_2O_5.*$$

$$1 \text{ c.c. of N/10 solution} = .007052 \text{ } Nb_2O_5.*$$

$$\text{Molecular weight } Nb_2O_5 = 267.$$

$$\text{Hydrogen equivalent of } Nb_2O_5 \text{ when reduced under the specified conditions} \quad \frac{.0267}{.007052} = 3.786.$$

* This result is the average of the values obtained for samples I_A , II_{3b} , II_1 & II_2 .

Moles of oxygen required to oxidize the product resulting from the reduction of one mole of Nb_2O_5 under the specified conditions
$$= \frac{3.786}{2} = 1.893.$$

$$5 - 1.893 = 3.107.$$

Therefore, Nb_2O_5 is reduced to $\text{Nb}_2\text{O}_{3.107}$, corresponding nearly to the oxide $\text{Nb}_{20}\text{O}_{31}$.

Reduction by Adding Zinc to the Solution.

It was thought that there might be some advantage in reducing the niobium solution in a flask with zinc instead of by means of the Jones reductor. A blank determination was therefore made on the zinc as follows: Eight grams of C.P. 20 mesh zinc was added to a flask containing 40 c.c. of concentrated sulphuric acid and 160 c.c. of water, heated to 70° or 80° C. and an atmosphere of carbon dioxide maintained. When the zinc was completely dissolved the solution was titrated in an atmosphere of carbon dioxide. Required 0.2 c.c. KMnO_4 .

A similar experiment using a solution containing .2000 grams of Nb_2O_5 required 3.3 c.c. of KMnO_4 , while it should have required nearly 30 c.c. if the reduction had been complete.

Another experiment using 10 grams of zinc and .2051 Nb_2O_5 , heated to 90° C. required 8 c.c. KMnO_4 .

Another experiment using 5 grams of 80 mesh zinc, and maintaining an atmosphere of hydrogen, required 1 c.c. of KMnO_4 solution for .1490 grams of Nb_2O_5 taken.

It was thought that perhaps the failure of these experiments in the reduction of the niobium was due to the fact that with the quite strong acid necessary in the solution the action on the zinc was so very rapid that the process could not continue for a sufficient time to effect any considerable reduction of the niobium without adding an excessive quantity of zinc.

Mixtures of Niobium and Tantalum.

Mixtures of Nb_2O_5 and Ta_2O_5 were next analyzed as indicated below:—

No.	Nb_2O_5 Taken	Ta_2O_5 Taken	Time minutes	KMnO_4 c. c.	Nb_2O_5 Found
(61)	.2051	.050	15	27.15	.1972
(62)	.2195	.050	8	29.90	.2171
(63)	.2039	.050	6	27.40	.1990
(64)	.2024	.100	9	27.50	.2001
(65)	.2008	.100	8	27.50	.1997
(66)	.1175	.100	12	15.80	.1148
(67)	.1098	.100	9	15.60	.1133
(68)	.1116	.100	5	15.10	.1097
(69)	.1394	.200	10	19.30	.1401
(70)	.1288	.200	6	17.00	.1235
(71)	.0513	.200	7	6.85	.0498

The Ta_2O_5 employed in these mixtures was passed through the reductor as a blank experiment and the potassium permanganate solution used in the titration (0.2 c.c.) deducted.

ANALYSIS OF MINERALS.

The method was next applied to the analysis of minerals, and for comparison, the minerals were also analyzed by the fractional crystallization method, details of which follow:

Crystallization Method.

Fuse 1 to 2 grams of the mineral with 8 to 10 parts of potassium bisulphate. Boil with water until completely disintegrated and filter, using a rubber funnel. Wash with hot water until the washings give only a faint test for sulphates. Wash on the funnel

with several portions (15 or 20 c.c. each), of yellow ammonium sulphide, hot, mixing on the filter as much as possible to get the best action. Wash with hot water until free from ammonium sulphide, then with dilute sulphuric acid to remove iron sulphide, then with hot water to remove sulphuric acid (the residue on the filter paper should now be pure white and contain nothing but silica, niobic and tantalic acids). Dissolve through the filter by means of warm dilute hydrofluoric acid.*

Add potassium fluoride approximately equivalent in weight to that of the sample taken. Evaporate on a water bath until the mass just solidifies on cooling. Dissolve in the smallest possible quantity of boiling hot water. Set aside to crystallize. The tantalum crystallizes as K_2TaF_7 , in the form of needles. The niobium crystallizes as $K_2NbOF_5 \cdot H_2O$, in the form of plates. These crystals must be carefully examined, using a magnifying glass if necessary, to determine whether they are needles or plates, or both. The first crop of crystals is nearly always needles, i. e., free from niobium. If there are no plates, filter on a small paper, using a rubber funnel, catching the filtrate in a platinum dish, and wash sparingly with water slightly acidified with hydrofluoric acid and containing about 1 gram of potassium fluoride per 100 c.c. Evaporate the filtrate to dryness exactly as before, take up in boiling water, etc., filtering off the needles (if free from plates) through the same funnel used for the first crop of crystals. This operation is repeated until a crop of crystals is obtained which consists of a mixture of needles and plates. When this mixture is obtained, add gradually a little of the wash water (one or two c.c. at a time), stirring until the plates disappear. Filter off the needles as before and wash sparingly with the washing solution. The filtrate should now contain all of the niobium and the crystals on the filter, all of the tantalum as

* Any dark colored residue indicates incomplete decomposition of the mineral and the residue must be ignited, fused and treated as before.

the double fluorides. Dissolve the tantalum salt from the filter, using boiling hot water and adding a few drops of hydrofluoric acid, the latter being necessary to prevent the formation of an insoluble tantalum compound. Add sulphuric acid to both the niobium and tantalum portions and evaporate to copious fumes of SO_3 to remove fluorides and boil with a considerable amount of water. Each element is precipitated by this boiling as its respective oxide, or hydrated oxide, insoluble in water. Filter, wash with hot water, ignite 10 minutes with a blast lamp, and weigh.

Remarks.—Evaporation of the fluoride solution must be carried on with great care, for if carried too far, the salts (especially the tantalum) are apt to become partially decomposed and thereby rendered insoluble in water. If evaporation is not carried far enough, too much hydrofluoric acid remains which would cause the niobium to crystallize in the form of prisms, instead of plates, which are difficult to distinguish from the needles of the tantalum salt.

Volumetric Method.

Fuse from 0.2 to 1.0 gram of the mineral with 5 to 10 grams of potassium bisulphate and proceed in exactly the same manner as with the crystallization method to the point of dissolving the precipitate from the paper with hydrofluoric acid. To the hydrofluoric acid solution, containing the niobium and tantalum, in a platinum dish, add 10 c.c. of concentrated sulphuric acid. Evaporate to copious fumes. Add a few c.c. more of sulphuric acid and repeat the evaporation to dense SO_3 fumes. Allow the solution to cool, and pour into cold water, washing the dish well, and add cold water to a volume of about 500 c.c. Heat to boiling and boil for a few minutes. Filter, wash with boiling water until only a faint test for sulphate. Ignite ten minutes with a strong blast and

weigh. This gives the weight of the combined oxides Nb_2O_5 Ta_2O_5 . Fuse with 5 grams of potassium bisulphate. Add 10 c.c. of concentrated sulphuric acid and heat gently to a clear solution. Transfer to a beaker, rinsing out the crucible with 30 c.c. of concentrated sulphuric acid. Allow to cool.* Add 2 grams of succinic acid and agitate, add about 20 c.c. of saturated aqueous solution of succinic acid in a fine stream from a wash bottle, keeping the solution in motion to assist solution of the succinic acid. Add water gradually to a volume of 200 c.c., constantly agitating the solution. Heat to 75°C ., reduce and titrate as described on page 9.

No.	Sample	Nb_2O_5 percent.	Ta_2O_5 percent.	Nb_2O_5 percent.	Ta_2O_5 percent.
(72)	A.	53.52	22.84	57.13	21.09
(73)	A.	54.06	22.69	56.82	21.30
(74)	A.	54.42	22.40		
(75)	A.	54.84	23.08		
(76)	B.	27.11	54.27	31.63	50.36
(77)	B.	27.44	53.91	30.24	51.24
(78)	C.	14.39	67.86	17.85	64.63
(79)	C.	14.30	68.26		64.41
(80)	D.	17.27	53.21	26.66	43.43
(81)	D.	16.48	53.92	27.03	43.98
(82)	D.	16.32			
(83)	D.	16.07			

Sample "D" contains quite large amounts of tin, difficult to separate from the niobium and tantalum, as experience has shown. This tin accumulates in the niobium portion in the crystallization method, thus causing high results for niobium. In the volumetric method the tin has no effect on the determination of niobium, but would cause the tantalum (estimated by difference) to be too high.

* Any cloudiness indicates incomplete decomposition of the oxides.

CRYSTALLIZATION METHOD						VOLUMETRIC METHOD			
No.	Mineral Taken	Nb ₂ O ₅ Found	Ta ₂ O ₅ Found	Nb ₂ O ₅ percent.	Ta ₂ O ₅ percent.	From Nb ₂ O ₅ portion Nb ₂ O ₅ Found	From Ta ₂ O ₅ portion Nb ₂ O ₅ Found	Nb ₂ O ₅ Total	Nb ₂ O ₅ percent.
(84)	.5873	.3294	.1136	56.09	19.35	.3164	.00289	.3193	54.37
(85)	.5737	.3198	.1185	55.77	20.19	.3089	.00723	.3161	55.10
(86)	.5264	.2995	.1080	56.89	20.05				

Comparison of Volumetric and Crystallization Methods.

Columbite A was analyzed again in triplicate by the crystallization method. The niobium and tantalum oxides obtained as a result of these analyses were individually fused and analyzed for niobium by the volumetric method giving results shown on page 18.

Nb_2O_5 is here shown to be present in the tantalum portion (as obtained by the crystallization method), and although no direct tests could be applied for the determination of the Ta_2O_5 in the niobium portion, the results of titration show beyond reasonable doubt that it was present.

The average of these volumetric determinations gives 54.73% for Nb_2O_5 , whereas the average of the results obtained by the regular volumetric method (page 17) is 54.21% Nb_2O_5 , sufficient evidence to show that the results obtained by the crystallization method are in error.

CONCLUSIONS.

1. A potassium sulphate-sulphuric acid solution of niobium and tantalum, to which succinic acid has been added, may be diluted considerably and heated without precipitation of compounds of either element.

2. The niobium of this solution may be reduced by passing the solution through a Jones reductor, after which the niobium may be determined volumetrically with potassium permanganate solution.

3. Neither the tantalum nor succinic acid are affected by the processes of reduction and oxidation as carried out in this method.

4. The temperature of the niobium solution during reduction should be 75° C., and the niobium should be titrated at once, the whole operation being carried out in an atmosphere of carbon dioxide.

5. The degree of amalgamation of the zinc used in the reductor is of great importance, the proportion adopted being 600 grams of C. P. 20-30 mesh zinc to 0.5 gram of mercury.

6. The method of fractional crystallization is at best only an approximate separation of niobium and tantalum. Some tantalum remains in solution with the niobium, and a little niobium is held by the tantalum.

7. The volumetric method gives lower results for niobium, and correspondingly higher results for tantalum, than the crystallization method.

8. The volumetric method is not extremely accurate, but is much more accurate than the method of crystallization, and may be carried out in considerably less time.

9. Under the conditions adopted the niobium is reduced to a degree indicated by the oxide $\text{Nb}_2\text{O}_{3.107}$ (i. e., 1 c.c. of N/10 potassium permanganate solution equals .007052 Nb_2O_5).

BIOGRAPHICAL.

Charles Edward Taylor entered Case School of Applied Science, Cleveland, Ohio, in September, 1902, was graduated in June, 1906, receiving the degree of B. S. Took up graduate work in chemistry at Columbia University in October, 1906, studied for the degrees of Master of Arts and Doctor of Philosophy, under the Faculty of Pure Science, until March, 1909, receiving the degree of Master of Arts in June, 1907.

